Measurements of Formaldehyde and Carbonyl Sulfide aboard R/V Atlantis during CalNex

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Introduction

Quantum cascade laser tunable infrared differential absorption spectroscopy (QCL-TILDAS) deployed during CalNex-2010 on the R/V Atlantis

Data used in the elucidation of atmospheric processes relevant to both climate change and air quality
Formaldehyde is *both* an accumulating product of oxidation and an inefficient reservoir of HOx

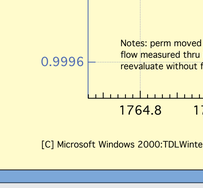
Formaldehyde formed via photo-initiated oxidation of methane and other hydrocarbons
emitted by combustion sources,, photolytic source of HOx indicator of processing in an aging air mass

Carbonyl sulfide (OCS) is the most abundant sulfur containing gas in the atmosphere. OCS is a surrogate for CO_2 uptake by plants during photosynthesis, but, unlike CO_2, is not emitted by plants during respiration

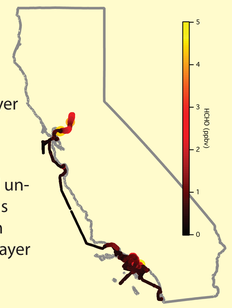
CalNex Campaign was ideal opportunity to measure HCHO

marine boundary layer oxidation chemistry
The ship sampled outflow of urban and continental air

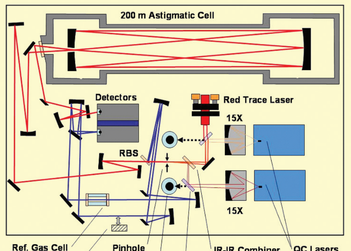
The complex flow pattern in the Los Angeles basin
city air was transported out above the marine boundary layer
mixed and advected back onshore

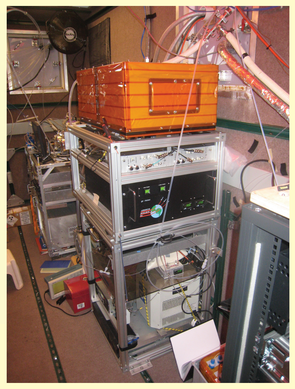


HCHO is useful when testing a model understanding chemical transformations taking place as the continental/urban plume ages in the marine boundary layer



QC Laser Based Absorption Spectroscopy





The absorption cell used high reflectivity mirrors coated formaldehyde (1765 cm^{-1}) and carbonyl sulfide (2052 cm^{-1})

known pathlength = 200.1 m Cell Pressure = 33-38 Torr
Sample Flow = 9.2 or 11.4 slpm

McManus *et. al*, Applied Optics 2011

Spectroscopic Calibration

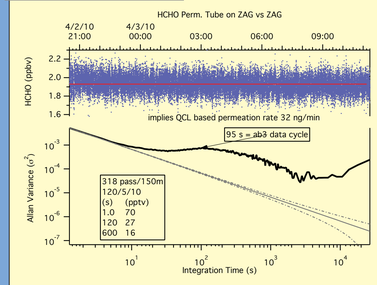
Direct sweep integration is used to collect transmission spectra and fit to Voigt lineshape. In principle this is an *absolute* measurement based on HITRAN 2008 line list parameters.

In-Field calibration and inlet assessment is performed ~hourly using stabilized permeation source delivery at the inlet

Comparison of instrument calibration with oxidation catalyst methods (using permeation device comparison) is excellent

At sea testing of the potential inlet/ozone senstivity along the 30' low pressure inlet and phase separation scheme
O_3 + inlet ⇨ HCHO
correction important in clean MBL air.
1.7±0.8 pptv HCHO ppbv^{-1} O_3

Instrument Performance

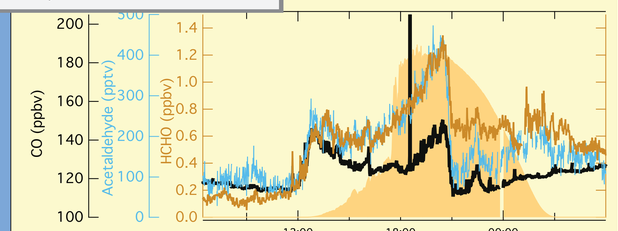


sub-70 pptv for the 1-s rms is demonstrated for this instrument at sea

laboratory performance is better and this had led to improvements in thermal stabilization and optical design.

Detection Limit is 6 fold improved from prior work

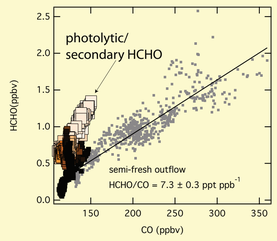
Photochemically Produced HCHO in outflow



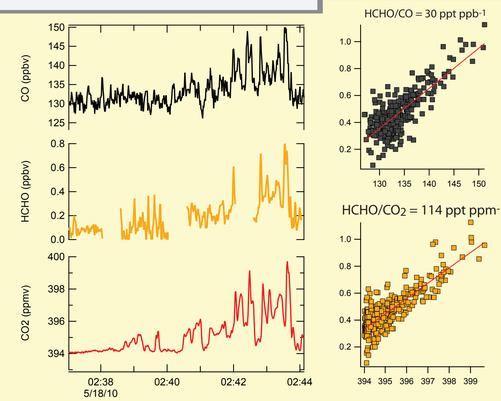
Primary urban HCHO/CO ratio is typically 3-4 pptv ppbv-1
Photo-oxidation chemistry in the presence of urban and biogenic VOCs tend to produce HCHO faster than HCHO is oxidized or photolyzed

The time-series depicts urban outflow sampled with and without sunlight

Initial HCHO/CO ratios typical in Atlantis/CalNEx are greater than other urban areas suggesting transport or non photolytic oxidation



HCHO in Ship Plume Exhaust



CO is typically the dominant non-CO_2 form of carbon from work producing combustion

This result compares well with previous studies which observed 5 to 50 ppt ppb^{-1}

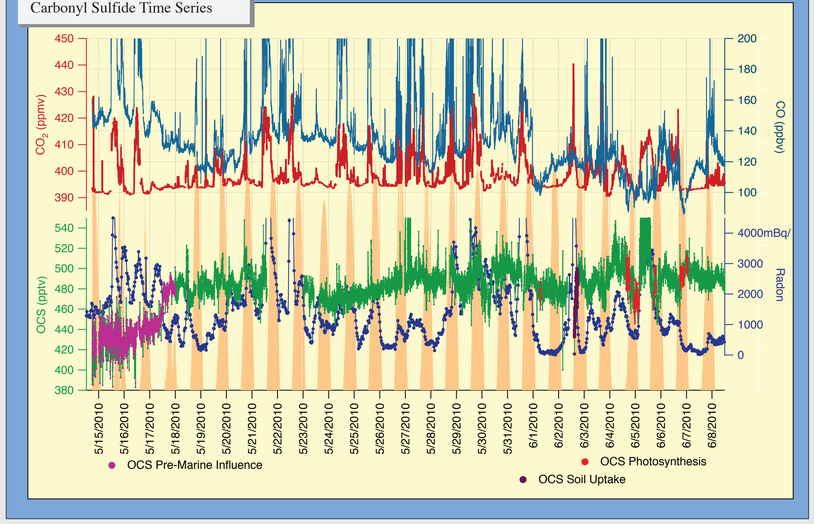
The idle plume from the Miller-Freeman depicted here is within the range of observations in TexAQS-II.

Controlled ship study indicates that HCHO EF is inversely correlated with NOx which is typical of work producing combustion

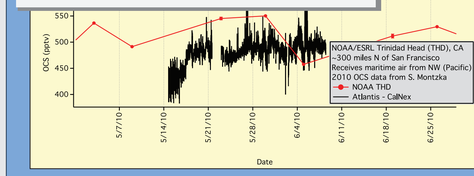
HCHO EF (mg/kg)
251±22 for slow speed hit
125±11 for medium
56±11 for fast
compares to HSC range (43-323 mg/kg)

Williams et al., JGR 2009

Carbonyl Sulfide Time Series



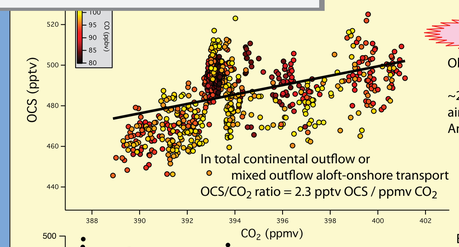
Carbonyl Sulfide comparison with coastal site



Similar range of variability in OCS data in the with weekly sampling data from Trinidad Head slightly less OCS? to the south during different synoptic weather pattern

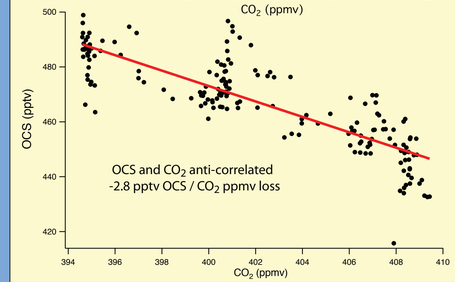
The fine structure in the high time resolution data will refine the understanding of using OCS as a biogenic tracer

Carbonyl Sulfide as tracer of biogenic exchange



Photosynthetic Uptake

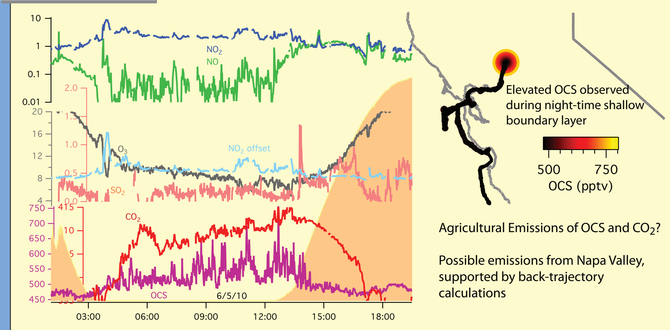
Observations in Atlantis data set comparable to OCS/CO_2 ratio ~2.5 pptv/ppm observed in June by aircraft measurements over North American (Montzka, 2007)



Soils Uptake

Evidence of Soil Uptake of OCS
- OCS loss during respiration over night on June 2nd-3rd.
- Ship situated to the north of Monterey Bay.
- Radon and CO_2 greatly increased (land-influence & vegetative respiration)
- OCS increased again with break-down of nocturnal boundary layer
- Comparable to OCS loss -3.2 pptv/ppmv observed at Harvard Forest in November with no photosynthetic uptake

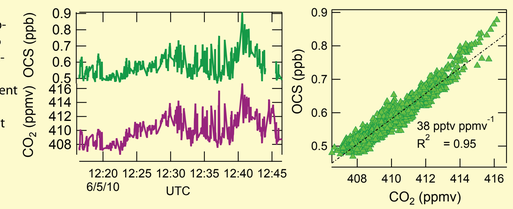
OCS Emissions



Agricultural Emissions of OCS and CO_2?

Possible emissions from Napa Valley, supported by back-trajectory calculations

Using the weak CO_2 absorption line nearby to the primary OCS detection feature, the CO_2 mixing ratio at equivalent time response can be determined. This event saw highly correlated OCS/CO_2



Conclusions

Quantum cascade laser (cw-QCL) enables 1 Hz measurement of formaldehyde and carbonyl sulfide

HCHO: excellent measurement performance, combines speed, sensitivity and accuracy

HCHO in offshore urban CO plumes suggests sufficient transport time for atmospheric oxidative chemistry

HCHO as primary emission in ship plues is verified and agrees with TexAQS-II measurments

OCS: Adequate Precision for Source Characterization (10 ppt Hz$^{-1/2}$)

OCS used to elucidate biogenic exchange, photosynthetic respiration and soi uptake

Tracer for large scale airmass changes

High time response measurements revealing previously uncharacterized sources

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Funded by NOAA Contract NA10AR4310101
Instrument support from DOE SBIR program

Ongoing Research

detailed analysis of HCHO in urban outflow

continued measurements of OCS at Harvard Forest